DECOLORIZATION OF DYE POLLUTANTS BY FENTON-LIKE OXIDATION PROCESS USING ZEOLITE AND NATURAL CLAY BASED CATALYSTS

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by

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Hamizura binti Hassan
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LIST OF SYMBOLS

λ	Wavelength	Unit
C_0	Initial concentration of dye	mg L^{-1}
C_t	Concentration of dye at reaction time	mg L^{-1}
A_i	The measured absorbance for components i	-
ε_λ	Molar absorptivity coefficient of solute at wavelength, λ	L (mg cm) $^{-1}$
C	Solute concentration	mg L^{-1}
t	Reaction time	min
T	Reaction absolute temperature	K
R^2	Coefficient of determination	-

LIST OF ABBREVIATIONS

US EPA	United States Environmental Protection Agency
AOPs	Advanced Oxidation Process
$Fe(OH)^{2+}$	Ferrous hydroxide
FeO(OH)	Ferric oxyhydroxide
$H_3O_2^+$	Peroxonium ion
$[Fe(H_2O)_6]^{3+}$ $[Fe(H_2O)_6]^{2+}$	Complex species
Fe-ZYT	Fe-contained zeolite Y type
Fe-BC	Fe-contained ball clay
Fe-NZ	Fe-contained natural zeolite
Fe-KKC	Fe-contained Kuala Kangsar clay
AR1	Acid Red 1
RB4	Reactive Blue 4
C.I.	Color index
DOE	Department of Environment
$Al_2(OH)_4$	Aluminum oxide/hydroxide
PILC	Pillared interlayer clay
BOD	Biological oxygen demand
COD	Chemical oxygen demand
TOC	Total organic carbon
SS	Suspended solids
BET	Brunauer-Emmett-Teller
FTIR	Fourier Transforms Infrared
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy

EDX	Energy Dispersive X-Ray
KBr	Potassium Bromide
BJH	Barret-Joyner-Halenda model
rpm	Rotation per minute
M	Molar
AAS	Atomic Absorption Spectrometric
IUPAC	International Union of Pure and Applied Chemists

PENYAHWARNAAN BAHAN PENCELUP MELALUI PROSES PENGOKSIDAAN JENIS FENTON MENGGUNAKAN MANGKIN ZEOLIT DAN BAHAN SEMULAJADI BERASASKAN TANAH LIAT

ABSTRAK

Penyahwarnaan bagi dua jenis bahan pencelup iaitu Acid Red 1 (AR1) dan Reactive Blue 4 (RB4) melalui proses pengoksidaan jenis Fenton menggunakan mangkin zeolit dan bahan semulajadi berasaskan tanah liat dalam sistem berkelompok dikaji. Pemangkin ini berjaya dihasilkan menggunakan teknik peranakan. Pencirian mangkin telah dijalankan menggunakan kaedah mikroskopi electron pengimbas (SEM), spektroskopi inframerah transformasi Fourier (FTIR), penjerapan/penyahjerapan nitrogen dan penyerakan tenaga x-ray (EDX). Kecekapan mangkin dalam proses penyahwarnaan bahan pencelup diuji melalui parameter-parameter seperti kesan ferum ion pembebanan di atas sokongan, dos bagi pemangkin, pH, kepekatan awal hidrogen peroksida dan bahan pencelup yang digunakan dan suhu bagi tindak balas. Di samping itu, penggunaan semula pemangkin dan jumlah ferum yang larut lesap dari pemangkin selepas proses penyahwarnaan turut dikaji. Melalui ujikaji penyahwarnaan secara berkelompok, keputusan menunjukkan tahap kereaktifan pemangkin bertambah sehingga mencecah tahap optimum bagi setiap peningkatan jumlah ferum ion pembebanan di atas sokongan, dos bagi pemangkin, suhu ujikaji, kepekatan awal hidrogen peroksida dan pengurangan nilai pH. Lebihan jumlah ferum ion pembebanan di atas sokongan, dos bagi pemangkin, suhu ujikaji, kepekatan awal hidrogen peroksida boleh mengakibatkan kesan pengaut kepada hidroksi radikal dan mengurangkan kadar penyahwarnaan. Keadaan terbaik yang diperolehi daripada proses penyahwarnaan bagi kedua-dua bahan pencelup ialah 0.60–1.0 wt.% bagi sokongan yang

mengandungi ferum, 2.50–5.0 g/L bagi dos pemangkin, pH dari 2.5–3.0 dan 8.0–20 mM bagi kepekatan awal hidrogen peroksida dengan menggunakan 50 mg L^{-1} kepekatan awal bahan pencelup pada 30 °C suhu tindak balas. Dengan keadaan terbaik, lebih dari 98% kecekapan penyahwarnaan bagi AR1 dan RB4 berjaya dicapai dalam masa 60 min hingga 210 min masa tindak balas. Jumlah ferum yang larut lesap dari semua pemangkin mematuhi Peraturan Alam Sekeliling (2009) bagi industri efluen bagi kedua-dua penyahwarnaan bahan pencelup. Keputusan tersebut menunjukkan bahawa mangkin heterogen mempunyai tahap stability dan aktiviti yang tinggi. Ternyata kepekatan ferum ion yang rendah boleh memberi kelebihan yang besar buat Fenton heterogen proses jika dibandingkan dengan homogen Fenton proses. Keputusan menunjukkan bahawa Fenton heterogen proses merupakan proses yang berkesan untuk penyahwarnaan AR1 dan RB4 bahan pencelup.

DECOLORIZATION OF DYE POLLUTANTS BY FENTON-LIKE OXIDATION PROCESS USING ZEOLITE AND NATURAL CLAY BASED CATALYSTS

ABSTRACT

The decolorization of Acid Red 1 (AR1) and Reactive Blue 4 (RB4) dye by the Fenton-like oxidation process using zeolite and natural based catalysts in batch system were studied. Fe-zeolite Y type (Fe-ZYT), Fe-natural zeolite (Fe-NZ), Fe-ball clay (Fe-BC), and Fe-Kuala Kangsar clay (Fe-KKC) were successfully prepared via impregnation method. The prepared catalysts were characterized by Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR), X-ray powder diffraction (XRD), Nitrogen adsorption/desorption and Energy Disperse X-ray (EDX). The effectiveness of these catalysts in the decolorization of the dye as well as the influence of reaction parameters like effect of iron loading on the supports, catalyst dosage, pH, initial concentration of hydrogen peroxide and dye and reaction temperature were assessed. Besides, the reusability and the amounts of iron leached from the catalyst after the reaction completed was evaluated. Through a number of batch decolorization experiments under various conditions, it is found that the activity of the catalysts increased until they reached an optimum value by increasing iron loading on the supports, catalyst dosage, temperature, initial hydrogen peroxide concentrations and decreasing the pH. The excess of iron on the supports, catalyst dosage and initial hydrogen peroxide concentration may lead to the scavenging effect of hydroxyl radical and decreased the decolorization rate. The best conditions obtained for the decolorization process for both dyes were 0.60–1.0 wt.% Fe-contained supports, 2.50–5.0 g/L of catalyst dosage, pH from 2.5–3.0 and 8.0–20 mM of initial concentration of hydrogen peroxide with 50 mg/L of

initial dye concentration at 30 °C reaction temperature. Under best conditions, more than 98% decolorization efficiency of AR1 and RB4 were achieved within 60–210 min reaction time. The amounts of iron leaching from all the catalysts prepared comply with the Environmental Quality (Industrial Effluents) Regulations, (2009) for both decolorization of AR1 and RB4. The result indicates that the heterogeneous catalyst had a long term stability and activity. Significantly lower concentration of iron ions in the bulk after the treatment could give a great advantage of the heterogeneous Fenton over the homogeneous Fenton type systems. The experimental results showed that the heterogeneous Fenton process was an effective process for the decolorization of AR1 and RB4 dyes.

CHAPTER ONE

INTRODUCTION

1.0 Introduction

In this chapter, a brief introduction on wastewater from textile industry that contains numerous types of dyes and chemicals are presented. These effluents create negative impacts on the environment and leads to the study on the new development of treatments that able to cope with the current situation. Problem statement, objectives and the organization of the thesis are also highlighted.

1.1 Textile Industry

The textile industry, apart from being an important contributor to the economy of numerous countries, is also a major source of various liquid, solid and gaseous wastes. This kind of industrial activity can have a negative impact on the environment, both in terms of pollutant discharge as well as of water and energy consumption (Fongsatitkul *et al.,* 2004). Textile mills are major consumers of water and consequently one of the largest groups of industries causing intense water pollution. Typically from 200 to 500 L of water are needed to produce one kg of finished product (Marcucci *et al.,* 2002; Colindres *et al.,* 2010). In addition, according to United States Environmental Protection Agency (US EPA), about (1 to 2) $x10^{-6}$ gal of wastewater per day are generated by average dyeing facility in the US. For instance, a relatively recent survey of the Malaysian textile industry has revealed that the volume of wastewater generated by dyeing and finishing operations ranged from 73 to 167 m^3 per ton of product (Lin *et al.,* 1996; Ahmed *et al.,* 2007). The amount of water used and wastewater generated is largely dependent upon the

specific type of operations followed. Generally dyeing, washing and finishing operations exert the greatest demand for water which generating most of the wastewater (Rodriguez *et al.,* 2002).

1.2 Dyes

There are numerous types of synthetic dyes like azo, vat, nitro, indigo etc, which are widely used for different purposes in textile industry (Neamtu *et al.,* 2002; Ashraf *et al.,* 2006). Around 10^6 tonne and more than 10,000 different synthetic dyes and pigments are produced annually worldwide and used extensively in dye industries (Akhtar *et al.,* 2005; Silveira *et al.,* 2009). There is a continual demand to develop longer, lasting, more applicable dyes. The development of synthetic fibers such as nylon, lycra, rayon and polyester has required the production of new dyes that can effectively bond to these materials. The United States Department of Commerce has predicted a 3.5 fold increase in textile manufacturing between 1975 and 2020 (Ganesh, 1992; Bandala *et al.,* 2008). Dyes must be continually updated to produce colors that reflect the trend dictated by changing social dyes and styles. Brighter, longer lasting colors are often necessary to satisfy the demand.

Effective cleaning of industrial wastewaters has become an increasingly concerning problems in the last decades. Modern legislation in many countries imposes environmental regulations and health quality standards that steadily become more restrictive (Zazo *et al.,* 2006). Dyes are considered an objectionable type of pollutant because they are toxic (Bae and Freeman, 2007) generally due to oral ingestion and inhalation, skin and dye irritation, and skin sensitization leading to problems like skin irritation and skin sensitization and also due to carcinogenicity

(Rai *et al.,* 2005; Christie, 2007). They impart color to water which is visible to human eye and therefore, highly objectionable on aesthetic grounds. In addition, they also interfere with the transmission of light and upset the biological metabolism processes which cause the destruction of aquatic communities present in ecosystem (Kuo, 1992; Gupta and Suhas, 2009). Further, the dyes have a tendency to sequester metal and may cause microtoxicity to fish and other organisms (Walsh *et al.,* 1980; El Qada *et al.,* 2006). As such it is important to treat coloured effluents for the removal of dyes.

The conventional wastewater treatment methods used for colored wastewater purifications are biological oxidation and physical-chemical treatment (e.g. coagulation-flocculation, and activated carbon adsorption). These processes are not sufficiently efficient since dyes are hardly removable due to their high molecular stability and water solubility. Another difficulty of these methods is that they are not destructive and they only transfer the contamination from one phase to another, causing the secondary waste and further treatments are deemed necessary (Benkli *et al.,* 2005). Biological treatment of wastewater is the most cost-effective alternative compared with other treatment options. Nevertheless, dye containing effluents are known to contain toxic and/or nonbiodegradable organic substances, so biological processes are not efficient in these cases (Daneshvar *et al.,* 2003).

1.3 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) represent an alternative when conventional wastewater treatment technologies are insufficiently effective. AOPs are destructive, low or non waste generating technologies involving the generation of

hydroxyl radicals in sufficient quantities to oxidize the majority of organics present in the water matrix. Thus, they are able to decolorize and to reduce recalcitrant pollutants in dye wastewater (Gogate and Pandit, 2004; Aleksić *et al.,* 2010). AOPs can be broadly classified into: chemical (e.g. Fenton process and/or O_3), photochemical and photocatalytic (e.g. UV/oxidant or UV/photocatalyst), mechanical (e.g. ultrasonic), and electrical (e.g. corona discharge) based on the energy applied for OH radical generation (Koprivanac and Kušić, 2007).

Fenton like processes offer cost effective source of OH radicals from H_2O_2 in the presence of iron cations and mild reaction condition and they are easy to operate and maintain (Tarr, 2003). Common homogeneous Fenton processes involve the application of ferrous or ferric salts and hydrogen peroxide in order to produce hydroxyl radical, as shown in the following equations (Centi *et al.,* 2000).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (1.1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \quad (1.2)$$

However, their overall efficiency is limited with a couple of disadvantages: (i) in some cases relatively high concentration of iron ions in the bulk may demand a secondary treatment and (ii) a Fenton catalytic cycle is restrained by the formation of stable Fe^{3+} complexes (Tarr, 2003; Aleksić *et al.,* 2010). Furthermore, Fenton type processes are typically maintained at low pH, which requires strong conditioning before and after the treatment, particularly in the case of dye house waste streams with pH in strong basic area (Hunger, 2002).

To overcome the disadvantages of the homogeneous Fenton process, and also considering the possibility of recovering the catalyst, some attempts have been made to develop heterogeneous catalyst, prepared by incorporating Fe ions or Fe oxides into porous supports (Letaief *et al.,* 2003; Ishtchenko *et al.,* 2003). In Fenton like system, the formation of hydroxyl radical is due to Fe^{2+} catalyzed decomposition of H_2O_2 on the surface of the support where the symbols ≡ represents the iron species bound to the surface of the catalyst.

$$\equiv Fe^{3+} + H_2O_2 \rightarrow \equiv Fe^{2+} + HOO^{\bullet} + H^{+} \quad (1.3)$$

$$\equiv Fe^{2+} + H_2O_2 \rightarrow \equiv Fe^{3+} + {}^{\bullet}OH + OH^{-} \quad (1.4)$$

In heterogeneous Fenton most of the reactions take place either at the surface of the supports or in the pores of the support, and only a very small portion occurred in the bulk. The reactions at the inner pores could be limited by double diffusion (H_2O_2 in and OH radicals out of the support pores). The hydroxyl radicals possess inherent properties that enable it to attack organic pollutants in water to obtain a complete mineralization into CO_2, water and mineral acids (Faure *et al.,* 2001; Esplugas *et al.,* 2002).

1.4 Problem Statement

The minimization of water pollution is one of today's main areas of scientific activity. Wastewaters which originated from dye production and application industries present a serious problem both from aesthetic and environment points of view. Therefore, dye wastewaters have to be treated prior to discharge in natural water bodies.

The Fenton like process are used as a powerful source of hydroxyl radicals from H_2O_2 in the presence of transitional metal cations, such as iron $Fe^{2+}/Fe^{3+}/H_2O_2$, to decompose many organic compounds including dye. However, the usage of homogeneous Fenton process has a number of disadvantages such as impossible regeneration of catalyst, requirement of narrow range of pH values for reaction and necessity of the treatment of the sludge containing iron before discharging it to receiving water (Dükkanci *et al.,* 2010).

These drawbacks can be overcome by using heterogeneous Fenton type catalysts. The crucial part in developing heterogeneous catalyst is associated with the stability of the catalyst. The iron oxide catalyst loses their activity because of leaching effects of metallic catalysts in acidic medium (Wu *et al.,* 2001; Liou *et al.,* 2005). An important point in the design of heterogeneous catalytic systems for advanced oxidation processes is the resistance of metal species to be leached into the aqueous solution under the oxidant and acidic conditions in which Fenton reactions usually precede. In this sense, a good supports must fulfill a number of requirements, such as high activity in terms of pollutants removal, marginal leaching of active cations, stability over a wide range of pH and temperature, and high hydrogen peroxide conversion with minimum decomposition (Larachi *et al.,* 1998).

In this work, the Fe-zeolite Y type (Fe-ZYT), Fe-ball clay (Fe-BC), Fe-natural zeolite (Fe-NZ) and Fe-Kuala Kangsar clay (Fe-KKC) was developed as new heterogeneous catalyst. The effectiveness of these catalysts was evaluated for decolorization of two types model pollutants which are acid red 1 (AR1) and reactive blue 4 (RB4) dye**.** The choice of AR1 and RB4 as model pollutant based on the fact

that they are typical dyes which are widely used in textile, pulp and paper industries. (Földváry and Wojnárovits, 2007). The influences of different reaction parameters such as different loading of iron on different supported catalysts, catalyst dosage, initial concentration of dye and H_2O_2 and initial pH and temperature on the decolorization efficiency were studied. In addition, the reusability of the catalysts and the concentration of iron ions in the bulk after the treatment were also evaluated.

1.5 Research Objectives

The main objectives of this research are to:

a) Develop the Fe-zeolite Y type (Fe-ZYT), Fe-ball clay (Fe-BC), Fe-natural zeolite (Fe-NZ) and Fe-Kuala Kangsar clay (Fe-KKC) as heterogeneous catalysts for decolorization of Acid Red 1 (AR1) and Reactive Blue 4 (RB4) dye solution in batch operation.
b) Characterize the prepared catalysts for their physical and chemical properties.
c) Study the influence of reaction parameters such as iron loading on the supported catalyst, catalyst dosage, initial concentration of dye and H_2O_2 and initial pH and temperature on the efficiency of the prepared catalysts.
d) Evaluate the leaching and reusability of the prepared catalysts.

1.6 Organization of Thesis

The earlier section of this chapter provides brief introduction to the current scenario of textile industry and its negative impact on the environment. The research background also presents conventional wastewater treatment and homogeneous Fenton methods that are inefficient to treat textile wastewater. This leads to the study

on the new development of heterogeneous catalyst that able to cope with the current situations.

Chapter two presents the characteristics of the textile wastewater and type of dyes commonly used in textile industries, and fundamental aspects of homogeneous Fenton process. It also gives a brief description on supports that were used in this study and parameters that affected the reaction process were discussed in detail.

Chapter three outlines the experimental work of research. It consists of list of materials and experimental methods used in this study. It outlines method of catalysts synthesis and methods to characterize the supported catalysts prepared. In addition, the experimental procedures in catalytic activity in batch process and for each of the reaction parameters are depicted in this chapter.

Chapter four focuses on physical and chemical properties of different prepared catalysts and its effect on decolorization efficiency of Acid Red (AR1) and Reactive Blue 4 (RB4). The effect of reaction parameters on the decolorization efficiency of AR1 and RB4 are discussed in detail. Evaluation of the reusability of the supported catalyst and the amounts of iron ions leached out from the supported catalyst are presented in this chapter.

Chapter five states some general conclusions, implications of this work and directions on future work. The experimental studies reported in this work provide useful information on long term stability of the prepared catalyst for the future application. Evaluations of physical and chemical properties of the prepared catalysts

give a good understanding about zeolite, ball clay, natural zeolite and Kuala Kangsar clay.

CHAPTER TWO

LITERATURE REVIEW

2.0 Introduction

Textile industry is the third largest foreign exchange earner after the electronic and palm oil industries in Malaysia, contributing total earning of RM 18.0 million (US$ 5.4 million) from manufactured exports in 2007 (Malaysian Textile Manufacturers Association, 2008). According to Firmino *et al.,* (2010), the textile industry represents 1.7% of world exportation in 2007 which corresponds to the amount of US$ 238.1 billions. There are about 1500 textile factories in Malaysia, mostly operate as backyard or cottage industries producing the local "batik". Textile processing consumes large amounts of water which in turn discharge large volumes of effluent. Color has been included in the water quality standards for the discharge of industrial effluents in Malaysia. Under the Environment Quality (Industrial Effluents) Regulations, 2009, the limits of colour for discharge of effluents according to standards A and B are 100 and 200 Platinum–Cobalt (PtCo) units, respectively (Lim *et al.,* 2010).

Textile effluents typically contain many types of dyes, detergents, solvents and salts depending on the particular textile process such as scouring, bleaching, dyeing, printing, and finishing (Barredo-Damas *et al.,* 2006). Main pollution in textile wastewater comes from dyeing and finishing processes. These processes require the input of a wide range of chemicals and dyestuff, which generally are organic compounds of complex structure. All the effluents are not contained in the final product and became waste and lead to disposal problems. In particular, coloured

effluents release into the environment is undesirable not only affect the aesthetics, the water transparency and the gas solubility in water bodies, but also due to the dyes breakdown products that are toxic, mutagenic or carcinogenic (Weisburger, 2002). Many dyes are difficult to biodegrade when discharge into waste streams since they have a synthetic origin and complex aromatic molecular structures. This aspect has always been overlooked in their discharge (Ho *et al.,* 2005).

2.1 Nature of Textile Effluent

Textile wastewater typically consists of different types of dyes, detergents, grease and oil, heavy metal, inorganic salts and fibers in amounts depending on the textile processing techniques (Lopez *et al.,* 1999; Lau and Ismail, 2009). The effluents are generally mainly characterized by the parameters such as biological oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), pH, color and suspended solids (SS) (Metcalf and Eddy, 2003). Typical characteristics of textile industries wastewater are presented in Table 2.1. For each of the parameters involved, a range of values is given, confirming the variability of the wastewater from the textile industry (Lau and Ismail, 2009). As presented in Table 2.1, COD values of composite wastewater are extremely high compare to other parameter and may be toxic to biological life. In most cases BOD/COD ratio of the composite textile wastewater is around 0.25 that implies that the wastewater contains large amount of non-biodegradable organic matter (Azbar *et al.,* 2004).

Table 2.1: Typical composite textile industry wastewater characteristics (Mehmet and Hasan, 2002)

Parameters	Values
pH	7.0-9.0
Biochemical Oxygen Demand (mg/L)	80-6000
Chemical Oxygen Demand (mg/L)	150-12000
Total Suspended Solids (mg/L)	15-8000
Total Dissolved Solids (mg/L)	2900-3100
Chloride (mg/L)	1000-1600
Total Kjedahl Nitrogen (mg/L)	70-80
Color (Pt-Co)	50-2500

Effluents discharged from textile dyeing and finishing industries are categorized as the most difficult to be disposed by biological, chemical and physical technologies. Those effluents from textile industries are generally high in organic contents and have a strong colour. In addition, those effluents also contain surfactants and additives which make them non-biodegradable as well as not meeting the effluent standards by the application of traditional activated sludge treatment which results into the serious environmental contamination (Shu *et al.,* 2005). So, the removal of dyes from the wastewater become of great importance and attracted a large number of research activities.

2.2 Classes of Dyes

There are many classes of dyes used during the dyeing process. The method of dye application and estimated degree of fixation for different of dye-fibre are described in Table 2.2.

Table 2.2: Method of dye application and estimated degree of fixation for different dye fiber combinations (Akbari *et al.,* 2002; Lau and Ismail, 2009)

Class	Characteristics	Substrates	Method of application	Fiber	Degree of fixation (%)
Acid	Anionic, water soluble	Nylon, wool, silk	Usually from neutral to acidic dyebaths	Polyamide	89–95
Basic	Cationic, water soluble	PAN, modified nylon, inks, polyester	Applied from acidic dyebaths	Acrylic	95–100
Direct	Anionic, water soluble	Cotton, rayon, leather, nylon	Applied from neutral or slightly alkaline baths containing additional electrolytes	Cellulose	70–95
Disperse	Very low water solubility	Polyester, polyamide, acetate, plastic, acrylic	Fine aqueous dispersions often applied by high temperature pressure or lower temperature carrier methods	Polyester	90–100
Reactive	Anionic, water soluble	Cotton, wool, silk, nylon	Reactive site on dye reacts with functional group on fiber to bind eye covalently under influence of heat and pH (alkaline).	Cellulose	50–90
Sulfur	Colloidal, insoluble	Cotton, rayon	Aromatic substrate vatted with sodium sulfide and re-oxidized to insoluble sulfur-containing products on fiber.	Cellulose	60–90
Vat	Colloidal, insoluble	Cotton, rayon	Water-insoluble dyes solubilized by reducing with sodium hydrosulfite, then exhausted on fiber and re-oxidized	Cellulose	80–95

Dyes are organic compounds consisting of two main groups of compounds, the chromophores, responsible for color of the dye, and the auxochromes, which can not only supplement the chromophore but also render the molecule soluble in water and give enhanced affinity (to attach) toward the fibers. Dyes exhibit considerable structural diversity and are classified in several ways. These can be classified both by their chemical structure and their application to the fiber type (Hunger, 2003). Dyes may also be classified on the basis of their solubility: soluble dyes which include acid, mordant, metal complex, direct, basic and reactive dyes; and insoluble dyes including azoic, sulfur, vat and disperse dyes (Christie, 2007).

On the other hand, either a major azo linkage or an anthraquinone unit also characterizes dyes chemically. It is worthwhile noting that the azo and anthraquinone dyes constitute about 70% and 15% of the total dyes produced, respectively and become the largest classes of dyes (Gupta and Suhas, 2009). Though, the classification of dyes on basis of structure is an appropriate system and has many advantages, like it readily identifies dyes as belonging to a group and having characteristic properties, e.g., azo dyes (strong, good all-round properties, cost-effective) and anthraquinone dyes (weak, expensive), there are a manageable number of chemical groups (about a dozen) (Acero *et al.,* 2002).

Reactive dyes are estimated to have the highest worldwide market share for different classes of dyes (Zollinger, 2003). Generally, reactive dyes which have the reactive groups enable them to react chemically with the fiber substrate to form a covalent bond (Lau and Ismail, 2009). In comparison to other classes of dyes, the degree of fixation of reactive dyes on the fabric is still very low where about 5–50%

of dyes remains in textile wastewater due to their incomplete exhaustion and dye hydrolysis in the alkaline dye bath during the dyeing processes (Table 2.2). The hydrolyzed dyes are derived when the reactive dyes react with water instead of reacting with the functional group of textile fabrics. The loss of dyes to the effluent, however, is dependent on the degree of fixation of the combination of different dye and fiber (O'Neill *et al.,* 1999).

Antraquinone reactive dyes are one of the major groups among reactive dyes other than azo compounds, based on the classification of molecular structures. In general, they are commercially applied as primary or secondary dyes in trichromatic dyeing formulations (Epolito *et al.,* 2005). Anthraquinone based dyes are more resistant to biodegradation due to their fused aromatic structures compared to azo based ones (Deng *et al.,* 2008). In addition, they may cause acute toxicity or even mutagenic effects on exposed aquatic organisms (Novotny´ *et al.,* 2006).

Acid Dyes were known from the past as synthetic dyes and were used for nylon, wool, silk, modified acrylics, and also to some extent for paper, leather, ink-jet printing, food, and cosmetics. They are generally water soluble. The principal chemical classes of these dyes are azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso (Gupta and Suhas, 2009).

According to the Color Index (C.I.), which is managed by the Society of Dyers and Colorists and the American Association of Textile Chemists and Colorists, currently more than 10,000 various types of dyes are synthesized and available in the world. Although no recent data is available on worldwide dye production, annual

production of over 700,000 tonnes has been often reported in the literature (Pearce *et al.,* 2003; Ozmen *et al.,* 2008). It is estimated that around 10–15% of dyes are wasted into the environment upon completion of their use in the dyeing unit which generates a strongly colored wastewater, typically with a concentration in the range of 10–200 mg/L (O'Neill *et al.,* 1999: Arslan-Alaton *et al.,* 2008). Release of some dyes in water streams has serious environmental impacts. Many of dyes can cause health problems such as allergic dermatitis, skin irritation, cancer and mutation in human. In addition, dyes absorb and reflect sunlight within water media and therefore hinder photosynthesis of aquatic plants (Chatterjee *et al.,* 2007; Pavan *et al.,* 2008). Thus, industrial dye-laden effluents are an increasingly major concern and need to be effectively treated before being discharged into the environment in order to prevent these potential hazards.

2.3 Environmental Quality (Industrial Effluents) Regulations 2009

In Malaysia, the discharge limits from wastewater treatment plant and industrial effluent is stipulated in the Fifth Schedule of Environmental Quality (Industrial Effluent) Regulations 2009. This regulation is under the Environment Quality Act 1974 for Standard A and B. Environmental Quality Act 1974 is an act relating to the prevention, abatement, control of pollution and enhancement of the environment, and purposes connected therewith. Table 2.3 shows the safety limits stipulated by Malaysian Government (DOE (Department of Environment), 2010).

Table 2.3: Parameters Limits of Effluents of Standards A and B (Environmental Quality (Industrial Effluents) Regulations 2009 under Environment Quality Act 1974) (DOE (Department of Environment), 2010)

Parameter	Unit	Standard	
		A	B
Temperature	° C	40	40
pH value	–	6.0–9.0	5.5–9.0
BOD_s at 20 °C	mg/L	20	50
Suspended solids	mg/L	50	100
Mercury	mg/L	0.005	0.005
Cadmium	mg/L	0.01	0.02
Chromium, Hexavalent	mg/L	0.05	0.05
Chromium, Trivalent	mg/L	0.20	1.0
Arsenic	mg/L	0.05	0.10
Cyanide	mg/L	0.05	0.10
Lead	mg/L	0.10	0.50
Copper	mg/L	0.20	1.0
Manganese	mg/L	0.20	1.0
Nickel	mg/L	0.20	1.0
Tin	mg/L	0.20	1.0
Zinc	mg/L	2.0	2.0
Boron	mg/L	1.0	4.0
Iron (Fe)	mg/L	1.0	5.0
Silver	mg/L	0.1	1.0
Aluminum	mg/L	10	15
Selenium	mg/L	0.02	0.5
Phenol	mg/L	0.001	1.0
Free chlorine	mg/L	1.0	2.0
Sulphide	mg/L	0.50	0.50
Oil and grease	mg/L	1.0	10.0
Colour	Platinum–Cobalt (PtCo)	100	200

2.4 Wastewater Treatment Technology

Government legislation is becoming more stringent in most developed countries regarding the removal of dyes from industrial effluent. This creates problem for the textile industries to comply with since the effluents from the textile industry commonly contain high concentrations of organic and inorganic chemicals which are characterized by very high COD, temperature, as well as strong color (Mantzavinos and Psillakis, 2004; Lim *et al.,* 2010). As such it is important to treat colored effluents for the removal of dyes. It must be emphasized that a wastewater treatment system is not just a process to cope with the environmental problem but also a step to recover valuable rinsed water as well as to minimize the waste volume discharged (Lau and Ismail, 2009).

Many chemical treatment processes have been used extensively to treat textile wastewater. Physical, chemical, and biological are presently available for treatment of wastewater discharged from various industries. However, physical methods such as liquid-liquid extraction, ion exchange, adsorption, air or steam stripping are ineffective because they simply transfer the pollutants to another phase rather than destroying them (Dutta *et al.,* 2001; Ramirez *et al.,* 2007). Activated carbon adsorption process for the removal of dyes is an accepted practice, but the cost of the treatment might be high (Georgi and Kopinke, 2005). Ozone and hypochlorite oxidations as well as UV radiation/hydrogen peroxide processes are efficient decolorization method, but they are not desirable because of high cost of equipment, operating cost and the secondary pollution arising from the residual chlorine. On the other hand, biological based processes (activated sludge, sequential bed reactors, anaerobic/anoxic) are widely used for textile wastewater treatment,

however with a rather limited success (Hao *et al.,* 2000). Although some of the more biodegradable dye auxiliaries may be completely eliminated from dyehouse effluents, the biological process cannot achieve "destructive" decolorization due to the fact that textile dyes are intentionally designed to resist biological, photolytic and chemical degradation. The nature of textile effluent depends on fashion, technical, technological, social and economic factors (Arslan-Alaton *et al.,* 2008)

Physical, chemical and biological method processes have different colour removal capabilities, capital costs and operating rates (Hamdaoui, 2006). These methods suffer from one or other limitations and none of them were successful in completely removing the color from wastewater (Sulak *et al.,* 2007). Therefore, it is necessary to find an effective treatment technology that leads to complete destruction of dye molecules, in terms of limited water resources management and the need for nature preservation. Table 2.4 shows the advantages and disadvantages of dyes removal methods.

Table 2.4: Advantages and disadvantages of dyes removal methods (Robinson *et al.*, 2001)

	Methods	Advantages	Disadvantages
Chemical Treatments	Oxidative process	Simplicity of application	(H_2O_2) agent needs to activate by some means
	H_2O_2 + Fe (II) salts (Fentons reagent)	Fentons reagent is a suitable chemical means	Sludge generation
	Ozonation	Ozone can be applied in gaseous state and therefore does not increase the volume of wastewater and sludge	Short half –life (20 min)
	Photochemical	No sludge is produced and foul odours are greatly reduced	Formation of by-products
	Sodium hypochloride (NaOCI)	Initiates and accelerates azo-bond cleavage	Release of aromatic amines
	Electrochemical destruction	No consumption of chemicals and no sludge build up	Relatively high flow rates cause a direct decrease in dye removal
Biological Treatments	Decolourisation by white-rot fungi	White-rot fungi are able to degrade dyes using enzymes	Enzyme production has also been shown to be unreliable
	Other microbial cultures (Mixed bacterial)	Decolourised in 24-30 h	Under aerobic conditions azo dyes are not readily metabolized
	Adsorption by living/dead microbial biomass	Certain dyes have a particular affinity for binding with microbialspecies	Not effective for all dyes
	Anaerobic textile-dye bioremediation systems	Allows azo and other water-soluble dyes to be ecolourised	Anaerobic breakdown yields methane and hydrogen sulphide
Physical Treatments	Adsorption by activated carbon	Good removal of wide variety of dyes	Performances dependents on wastewater characteristics
	Membrane filtration	Removes all dyes types	Concentrated sludge production
	Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
	Irradiation	Effective oxidation at lab scale	Requires a lot of dissolved O_2
	Electrokinetic coagulation	Economically feasible	High sludge production

2.5 Advanced Oxidation Processes (AOPs)

Advanced oxidation processes (AOPs) have emerged as interesting alternative for the destruction of organic pollutants in industrial wastewater and are extremely useful in the case of substances resistant to conventional technologies. AOPs processes are combination of ozone (O_3), hydrogen peroxide (H_2O_2) and UV irradiation, which showed the greatest promise to treat textile wastewater (Joseph *et al.,* 2009). These oxidants effectively decolorized dyes however did not remove COD completely (Ahmet *et al.,* 2003; Arslan-Alaton *et al.,* 2008).

AOPs are based on the generation of highly reactive hydroxyl radicals ($^{\bullet}OH$) that are very effective in degrading organic pollutants because of their strong oxidant power ($^{\bullet}OH + H^+ + e^- \rightarrow H_2O$; $E^o = 2.80$ V) and nonselective species (Chan *et al.,* 2003; Li *et al.,* 2010). Table 2.5 shows the relative oxidation potentials of several chemical oxidizers.

Table 2.5: Oxidizing potential for conventional oxidizing agents (Li *et al.,* 2010)

Oxidizing agent	Electrochemical oxidation potential (EOP), V	EOP relative to chlorine
Flourine	3.06	2.25
Hydroxyl radical	2.80	2.05
Oxygen (atomic)	2.42	1.78
Ozone	2.08	1.52
Hydrogen peroxide	1.78	1.30
Hypochlorite	1.49	1.10
Chlorine	1.36	1.00
Chlorine dioxide	1.27	0.93
Oxygen (molecular)	1.23	0.90

Advanced oxidation processes are characterized by production of $^{\bullet}OH$ radicals and non selectivity of attack which is useful attribute for an oxidant. The versatility of AOP is also enhanced by the fact that they offer different possible ways for $^{\bullet}OH$ radicals production thus allowing a better compliance with the specific treatment requirements (Khatee *et al.,* 2009). A list of the different possibilities offered by AOP is given in Table 2.6. Generation of $^{\bullet}OH$ is commonly accelerated by combining O_3, H_2O_2, TiO_2, UV radiation, electron-beam irradiation and ultrasound. Among these combinations, Fenton and UV/Fenton type process holds the greatest promise to oxidize textile wastewater (Mahmoud *et al.,* 2010).

Table 2.6: Different possibilities offered by advanced oxidation processes (AOP) (Andreozzi *et al.,* 1999; Al-Kdasi *et al.,* 2004)

Combination
$H_2O_2/UV/Fe^{2+}$ (Photo assisted Fenton)
H_2O_2/Fe^{2+} (Fenton)
Ozone/UV (also applicable in the gas phase)
Ozone/ H_2O_2
Ozone/UV/ H_2O_2
Ozone/TiO_2/Electron-beam irradiation
Ozone/ TiO_2 /H_2O_2
Ozone + electron-beam irradiation
Ozone/ultrasonics
H_2O_2/UV

2.6 Fenton's Reagent

Fenton's reaction is a homogeneous catalytic oxidation process using a mixture of hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) in an acidic medium, which was firstly discovered by Fenton in 1890 (Sun *et al.,* 2008). In the last decades, Fenton reaction has been introduced into wastewater treatment processes, and it has been well proven that a refractory organics could be effectively degraded through Fenton's reaction without producing any toxic substances in water environment (Neyens and Baeyen, 2003; Pera-Titus *et al.,* 2004; Sun *et al.,* 2009).

Fenton oxidation process is performed in four stages, which are pH adjustment to low acidic values, oxidation reaction, neutralization and coagulation. At pH lower than 3.5, H_2O_2 and Fe^{2+} are more stable resulting in redox system and decolorizing better. However, at pH values higher than 4.0, ferrous ion easily form ferric ions which have a tendency to produce ferric hydroxo complexes. H_2O_2 is unstable and easily decompose itself in basic (pH>10) solutions (Kuo, 1992; Meriç *et al.,* 2004). The mechanisms that describe Fenton's reaction mainly include the following reaction: (Malik and Saha, 2003)

The ferrous ion (Fe^{2+}) reacts with H_2O_2 to produce hydroxyl radical ($^{\bullet}OH$).

$$H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + OH^- + Fe^{3+} \quad (2.1)$$

$^{\bullet}OH$ may react with Fe^{2+} to form ferric ions (Fe^{3+}) or react with organics compounds.

$$^{\bullet}OH + Fe^{2+} \rightarrow OH^- + Fe^{3+} \quad (2.2)$$

$$^{\bullet}OH + \text{Organics} \rightarrow \text{Product} \quad (2.3)$$

$^{\bullet}OH$ generation is enhanced at low pH (2.5-4.5). The oxidation products are usually low molecular weight oxygenated compound that are easily biodegradable (Parka *et al.,* 2001: Malik and Saha, 2003) or in some instances, the organic compounds reduce to carbon dioxide and water (Dutta *et al.,* 2001).

$^{\bullet}OH$ can react with H_2O_2 to produce other radicals which is hydroperoxyl radical ($HO_2^{\bullet}$), and may also combine with each other to produce H_2O_2.

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (2.4)$$

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \quad (2.5)$$

Ferrous ions and radicals are produced during the reactions (Eqs. (2.6) to (2.9)).

$$H_2O_2 + Fe^{3+} \leftrightarrow H^+ + FeOOH^{2+} \quad (2.6)$$

$$FeOOH^{2+} \rightarrow HO_2^{\cdot} + Fe^{2+} \quad (2.7)$$

$$HO_2^{\cdot} + Fe^{2+} \rightarrow HO_2^- + Fe^{3+} \quad (2.8)$$

$$HO_2^{\cdot} + Fe^{2+} \rightarrow O_2 + Fe^{3+} + H^+ \quad (2.9)$$

The reaction rate in Eq. 2.6 is much slower than that in Eq 2.1. Generally, Fe^{2+} consumed quickly, but reproduces slowly (Pignatello, 1999). Consequently, the oxidation rate of organic compounds is fast when large amounts of ferrous ions are present because large amount of hydroxyl radicals are produced. However, the Fenton's reaction may slow down due to the slow ferrous ion production (Benitez *et al.,* 2007).

The generation of hydroxyl radicals in the Fenton reaction has been used in a variety of processes: (1) homogeneous Fenton process, involving iron(II) salts

dissolved in an acid medium, (2) heterogeneous catalysis (Fenton-like reaction), (3) photo-reduction of Fe(III) to Fe (II) through the use of ultraviolet radiation (photo-Fenton process (De Oliveira *et al.,* 2007) (4) electro-oxidation and photo-electron oxidation (Sirés *et al.,* 2007; Ting *et al.,* 2007) and (5) nanocatalyst (Joo and Zhao, 2008; Garrido-Ramírez *et al.,* 2010).

The efficiency of the Fenton oxidation process depends on the H_2O_2:organic carbon ratio, organic matter content, temperature and Fe(II) concentration (Lin & Lo, 1997; Guedes *et al.,* 2003). Depending on the effluent being treated, different operating conditions should be employed to achieve high degradation efficiencies. The pH, Fe(II):H_2O_2 ratio and H_2O_2 concentration are also crucial in Fenton oxidation process (Kang *et al.,* 2000; Guedes *et al.,* 2003).

2.6.1 Disadvantages of Homogeneous Fenton's Reaction

The homogeneous Fenton process has been widely investigated. This simple process uses conventional equipment and operates at ambient temperature and pressures. The process however has some drawbacks due mainly to the formation of different Fe(III) complexes as solution pH changes. The optimum pH for the homogeneous Fenton process is about 2.8 when the iron in solution occurs partly as Fe(III) and partly as $Fe(III)(OH)^{2+}$, representing the photo-active species. Below this pH, the hydroxyl radical are scavenged by protons and the concentration of $Fe(III)(OH)^{2+}$ declines above this pH and Fe(III) precipitates as an oxyhydroxide (Bobu *et al.,* 2008). On the other hand, in order to maintain the pH of ~3, large amounts of acids (usually sulphuric acid) must be added to the reaction medium (Valdés-Solís *et al.,* 2007). Thus, it is impractical to apply the homogeneous Fenton